Conductometric Sensor Based on Nanostructured Titanium Oxide Thin Film Deposited on Polyimide Substrate with Dissimilar Metallic Electrodes

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***Abstract*— A conductometric sensor was fabricated on flexible polyimide substrate with using interdigital transducer (IDT) formed by periodic Au and Cr tracks and coated with a TiO_2 nanostructured sensitive layer. Thin films of TiO_2 were deposited using the radio frequency (RF) magnetron sputtering method. Atomic force microscope (AFM) and scanning electron microscope (SEM) techniques were employed for the characterization of thin films. The sensor was tested towards humidity changes at room temperature.**

Keywords- TiO_2, moisture sensing, flexible substrate, polyimide

I. Introduction

The most common and economically destructive form of corrosion is the rusting of iron. About 25% of the steel produced in U.S. is made to replace corroded objects [1]. The water droplets condensed on the surface of the paint, as well as the salt (NaCl) stays on the surface could form ionic solutions, which accelerates the rusting of steel material. Thus, it is of significant importance to develop sensors capable of detecting low concentrations of moisture surrounding the surface.

Recent advances in the development of nanostructured catalysts such as metal oxide nanoparticles, nanotubes, nanowires, nanorods, and nanobelts [2-5], provide the opportunity to greatly increase the sensitivity of these materials, as sensor performance is directly related to granularity, porosity and ratio of surface area to volume in the sensing element. It has been established that the sensitivity of semiconductor metal oxide gas sensors increases with decreasing grain size [6]. Thus, low dimensional nanostructured materials, which have an increased surface to volume ratio when compared to conventional polycrystalline structures, facilitate rapid diffusion of gases into and out of the materials' nano- and microporosities. This in turn increases the reaction rate, resulting in faster sensor response and recovery time of the sensor. Semiconductor metal oxide thin films also offer low cost, consistent performance and easy fabrication [7].

TiO_2 has been greatly exploited for its sensing properties towards moisture, thus leading to its use in humidity sensors [8]. Different deposition techniques, such as sputtering, sol-gel, and chemical vapor deposition are widely employed for the fabrication of TiO_2 thin film based sensor [8-11].

In this paper, RF magnetron sputtering is utilized for depositing TiO_2 thin film to operate as a sensitive media layer. In addition, in order to achieve mechanical flexibility, polyimide was chosen to from the sensor substrate due to its flexible and corrosion-resistive properties. Therefore, the sensor can be installed on both rigged and flexible surfaces.

II. Fabrication

The IDT of the sensor are formed by interchanging finger pairs of two different types of metal, Au and Cr (which can also generate electric potential when the surface media contains sufficient charge carriers). The IDTs are coated by a TiO_2 sensitive layer which is employed as the sensitive media to provide extra charge carriers when the sensor is exposed moisture.

The sensor was fabricated on polyimide substrate by using a two-cycle exposure and etching photolithographic method. A two mask patterning process was employed to fabricate each sensor. The two mask patterns (positive and negative) are shown in Figure 1.

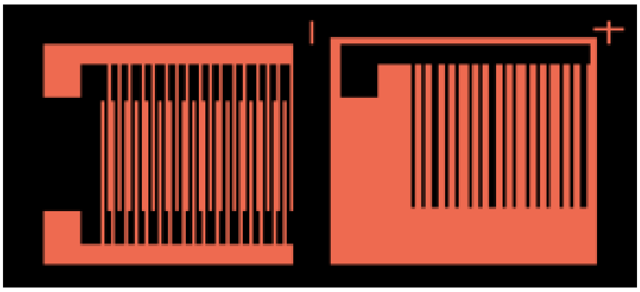

Figure 1. Positive (left) mask and negative (right) mask designed for fabricating the sensors.

The polyimide substrate was coated by Cr and Au (in order of deposition), both with thickness of 50 nm. After AZ1512 photo-resist was spin coated onto the substrate, the samples were baked at 90ºC (soft baking) for 20 min. At the first cycle of this lithography method, the positive mask was used for transferring the pattern onto the substrates. AZ400 (1:4 mixed with deionized (DI) water) developer was then used for developing the finger paired pattern. Next, the samples were baked again at 110ºC (hard baking) for 20 min. Initial etching was carried out by etching both Au and Cr layers. As soon as the photo-resist was removed from the metallic tracks, the first cycle was ready. In the second cycle, every procedure was repeated, except by using of the negative mask and Au etching only. During the exposure, the negative mask protected one side of finger pairs and after removing Au layer, one side of the finger pairs was left with the Cr tracks only, while the other side is still covered by Au. The schematic representation of the photolithography process is shown in Figure 2.

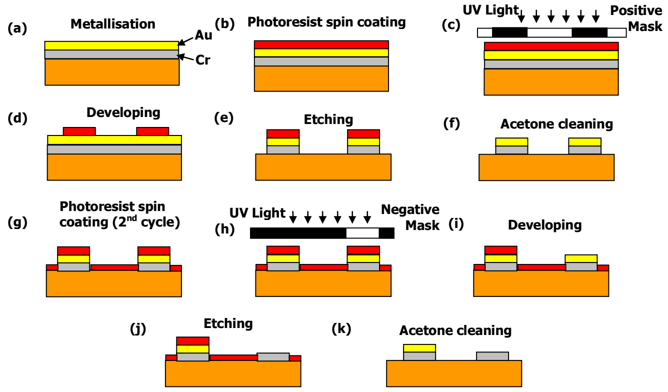

Figure 2. A schematic representation of the photolithography process.

TiO_2 films were deposited using a 99.9% pure Ti target by RF magnetron sputtering in an Ar (20%) and balanced in O_2 for 30 min at room temperature. A chamber pressure of 2.5×10^{-5} torr and RF power of 90W was used for sputtering. The sputtered TiO_2 film layer has a thickness of approximately 200 nm.

TiO_2 was doped using a NaCl solution by soaking the surface with a droplet of NaCl solution (5 mg/ml) and then annealed. The doping is required to reduce the sputtered TiO_2 sensitive layer's resistance to mega Ohm range.

III. STRUCTURAL CHARACTERISATION

Atomic force microscope and scanning electron microscope were employed for surface and structure analysis. Using AFM, the surface of polyimide, TiO_2 layer on polyimide, TiO_2 layer on Au metallic tracks, as well as TiO_2 layer on Cr metallic tracks were imaged and analyzed. The AFM image of polyimide surface is shown in Figure 3 and the TiO_2 layers on polyimide, Au electrode and Cr electrode are illustrated in Figure 4, 5 and 6, respectively.

From the AFM image, low surface roughness (9.6 nm) of the polyimide substrate can be observed; the grain size is around 0.1 µm. When TiO_2 layer was deposited onto the polyimide substrate, the grains were almost uniformly distributed; the surface roughness increases to 36.5 nm, which provide increased surface area to volume ratio for gas sensing. The TiO_2 layers were quite similar when it was deposited on Au and Cr electrodes, hill like structures with significant height differences and sharper tips were observed (surface roughness of 17.1 nm); similar TiO_2 structures with lower surface roughness (16.4 nm) were obtained on Cr tracks.

The SEM images of the TiO_2 film on Au are shown in Figures 7 and 8 which are consistent with AFM results. However, cracks were observed on TiO_2 films which deteriorate the performance of the sensors. It appears that the cracks are the sites where the hill like structures are observed in the AFM images.

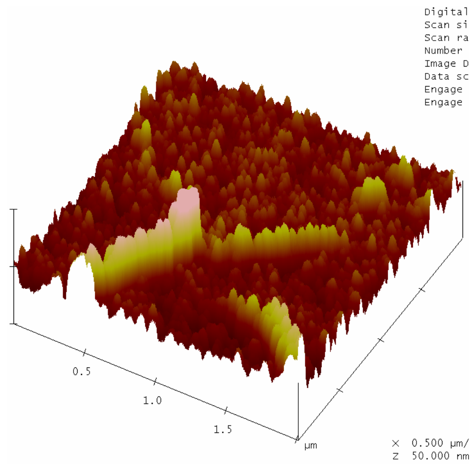

Figure 3. Polyimide surface image

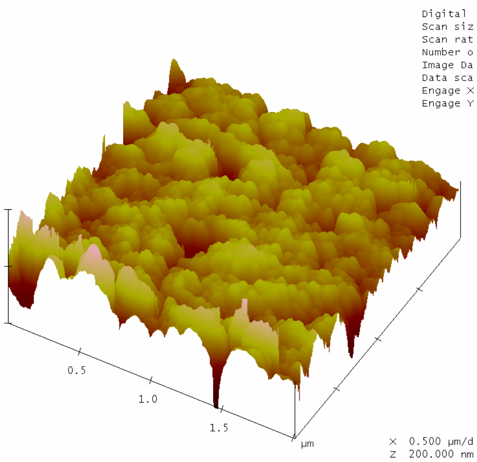

Figure 4. TiO_2 on polyimide surface

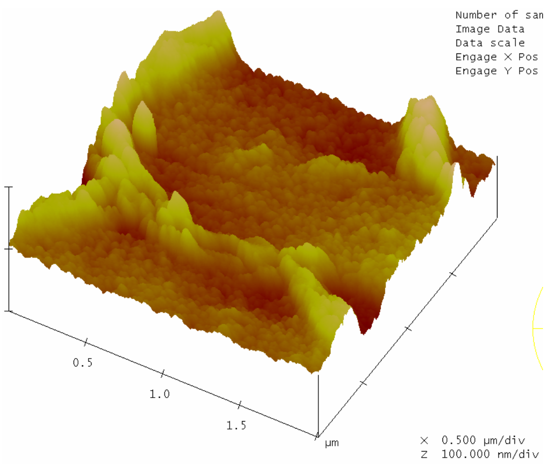

Figure 5. TiO_2 on Au electrodes.

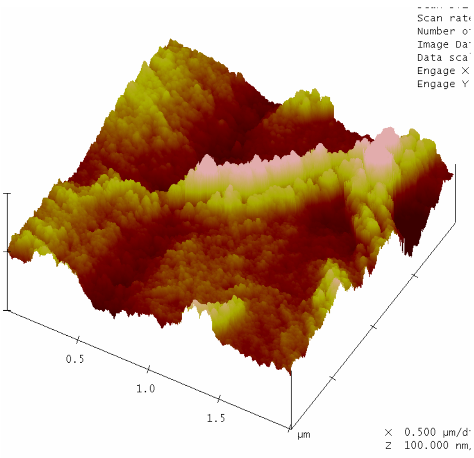

Figure 6. TiO_2 on Cr electrodes.

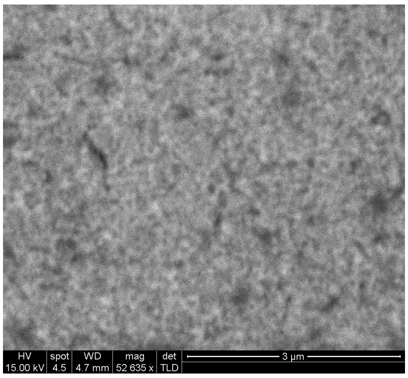

Figure 7. SEM image of TiO_2 film on Au electrode

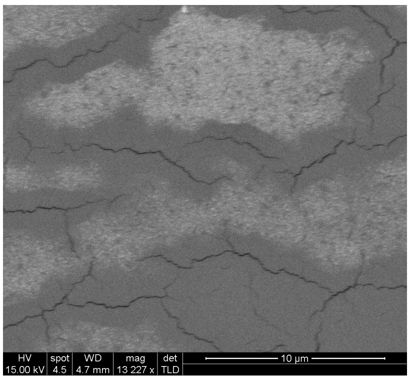

Figure 8. SEM image of TiO_2 film on both Au and Cr electrodes

IV. Electrical Testing

Preliminary testing shows, the sensor is highly sensitive to humidity changes, even a brief exhalation of human can largely affect its two-wire resistance. During the testing, the sensor is placed into a gas chamber while dry air and wet air were supplied (varying relative humidify from 42% to 79%) at room temperature. The resistance decreases and increases when the sensor was exposed under wet air and dry air, respectively. The humidity response is shown in Figure 9. Further investigations into the surface performance under these conditions are currently being undertaken.

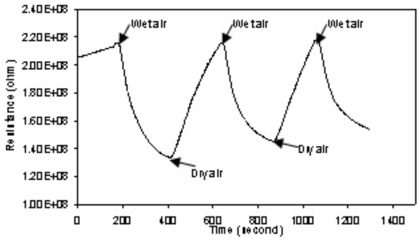

Figure 9. Response to humidity changes.

V. Conclusion

Humidity sensors were successfully fabricated on polyimide substrates. TiO_2 nanostructured sensing layers were deposited using RF sputtering technique. The film was characterized using SEM and AFM techniques. The transducers were tested as humidity sensors at different relative humidity. The sensor proved to have significant commercial value for moisture monitoring as it is mechanically flexibility; has low weight, and low fabrication cost.

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